



## Regular article

## Correlation between vanadium carbide size and hydrogen trapping in ferritic steel

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## ABSTRACT

Hydrogen trapping on vanadium carbides (VC) was studied in a low-carbon ferritic steel. Thermal desorption analysis was performed on two conditions with different carbide sizes but identical volume fractions. Smaller carbides with a higher effective surface area trapped significantly more hydrogen. A correlation between carbide size and hydrogen trap density was established, suggesting that trapping is surface-dominant and a scaling law for trap density was derived. The amount of trapped hydrogen was overall much lower than previously reported for VC-containing martensitic steels. It is therefore suggested that in the absence of a dislocated matrix VC traps relatively little hydrogen.

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In recent years there has been much interest in transition metal carbides as microstructural traps for mitigating hydrogen embrittlement in steels [1–5]. In service conditions with limited exposure to hydrogen, carbides can bind most of the highly mobile lattice hydrogen which has been shown to be the main cause of embrittlement [6]. Among all the carbides vanadium carbide has received the most attention because of the relatively low price of vanadium compared to other carbide formers (e.g. W, Mo) and its relatively low formation energy which facilitates precipitation control. We hereafter refer to vanadium carbide as VC, making no distinction between the different observed stoichiometries and crystallographic structures [7]. While it is proven that carbides reduce embrittlement problems, the mechanism is unclear. The main issue is that trapping energies derived from experiments and first-principles calculations are low (below 30 kJ mol<sup>-1</sup> and 15 kJ mol<sup>-1</sup>, respectively [3,8]), which is in the range of other weak traps such as dislocations or grain boundaries. This means that under the assumption of local equilibrium [9], even high carbide densities should only be able to absorb a relatively small fraction of the harmful lattice hydrogen. The amount

of hydrogen absorbed by carbides also seems to depend strongly on their structure and distribution. It has been argued that incoherent carbides are more effective as traps compared to coherent ones [10,11], but conflicting arguments have emerged regarding the exact location of trapping – the bulk [12] or both the bulk and the interface [11]. The evidence so far suggests that there should be a carbide size, which offers both a large degree of incoherency but maximizes the total surface area of carbides given a constant volume fraction. To this aim we studied a ferritic steel with VC precipitates, heat treated to diminish the effect of other potential traps in order to isolate VC as the only relevant trapping site and explore the effects of their size and morphology on hydrogen trapping. Optical and transmission electron microscopy (TEM) were used to characterise the microstructure and carbides, respectively.

The composition of the steel was 0.08 C, 0.021 Al, 0.76 Mn, 0.0033 N 0.26 V in wt% and heat treatments used to obtain various VC morphologies were first modelled in the precipitation modelling suite MatCalc, version 5.62 using the iron thermodynamic database version 2.009, the diffusion database version 2.008 and the physical properties database version 1.03. Several options were explored to reduce cementite and martensite formation, before settling on a heat treatment composed of an austenitisation step followed by annealing. Austenitising at 1200 °C ensured full dissolution of all phases and during annealing VC precipitated volumetrically in ferrite until vanadium was depleted. Upon cooling to room temperature

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the remaining carbon, concentrated in austenitic grains, transformed into pearlite. According to simulations, annealing below 740 °C did not lead to further VC refinement so this temperature was chosen as the lower limit. This treatment is referred to as LT and the VC structure resulting from it are shown in Fig. 1. The 800 °C annealing (referred to as HT) was chosen because no precipitation in austenite was predicted due to the low C and V content – the fraction of ferrite thus had to be kept sufficiently high to achieve uniform precipitation while keeping the temperature high enough to accelerate coarsening. 800 °C was chosen as a compromise between both. The austenitisation and annealing steps lasted 15 min and 1 h, respectively, followed by air cooling to room temperature. Fig. 1 also displays the simulation results which suggest the two treatments produce two distinct carbide sizes and number densities while having nearly the same VC volume fractions.

The steel was spark-machined into cylinders of 8 mm in diameter and 12 mm in height. They were wrapped in a stainless steel sheet, to reduce oxidation, and heat-treated. For hydrogen charging they were given a 1200 grit manual finish, then spark-welded onto a three-pronged stainless wire holder and ultrasonically cleaned in an acetone bath for 2 min. The cylinder ends and wires were coated with a layer of non-conducting varnish to prevent hydrogen ingress on cylinder faces and the holder. The holder itself was axis-symmetrical with prongs at 120° in order to minimise variations in charging conditions between the three samples. The charging solution consisted of 2 l of deionised water with 70 g of NaCl and 6 g of NH<sub>4</sub>SCN as a hydrogen recombination inhibitor. The charging was performed with a Gamry Interface 1000E galvanostat under a current density of 10 mA cm<sup>-2</sup> for 96 h using a platinum coil counterelectrode. The driving voltage oscillated around -2 V and no signs of corrosion were observed during charging. After completion, the specimens were rinsed with deionised water and immediately stored in liquid nitrogen to prevent hydrogen effusion. Thermal desorption analysis (TDA) was performed in an Agilent 7890B rig – the samples were removed

from liquid nitrogen and given an ultrasonic acetone bath for 1 min. They were transferred to the rig which had to be purged for 30 min before the start of the experiment, thus allowing some hydrogen to effuse from the samples. For TEM imaging the cylinders were cut into sections, manually ground to 100 μm and punched into 3 mm disks. These were ground to 50 μm on 1200 grit paper and electropolished to produce TEM samples. The imaging was done on a FEI F20 microscope at 200 kV.

Fig. 2 shows carbides in the two annealing conditions (a, b and d, e) and an EDX scan (c) showing vanadium distribution. The carbides in the LT sample are more faceted and elongated compared to the more spherical carbides in the HT condition. Particle area and count were measured and their average values are shown in Table 1. Surprisingly, the HT carbides are smaller than the LT ones, which could be explained by carbon segregation into austenite during annealing – at 800 °C the simulations suggest an equilibrium austenite volume fraction of 19%, compared to 5% at 740 °C, which can result in reduced carbon availability for precipitation at 800 °C. The second important observation is that while the average HT carbide radius of 5.5 nm is somewhat close to the predicted value, the LT radius of 7.9 nm is significantly larger than expected, suggesting that coarsening is in fact much faster than predicted, hindering precipitation control. The experimental number densities are inversely related to the average radii as expected. The measured amount of pearlite is higher in the HT condition because of the higher austenite fraction during annealing at 800 °C, but is quite low nonetheless. Its presence should not contribute significantly to trapping as even in fully pearlitic steels pearlite absorbs less than 1 wppm hydrogen [13,14].

The measured number densities seem inaccurate – using them to calculate the VC volume fraction yields values over twice the limit imposed by the vanadium content, which is 0.43%. Since TEM radius measurements are fairly reliable it appears that the number density measurements were skewed due to the limitations of TEM particle

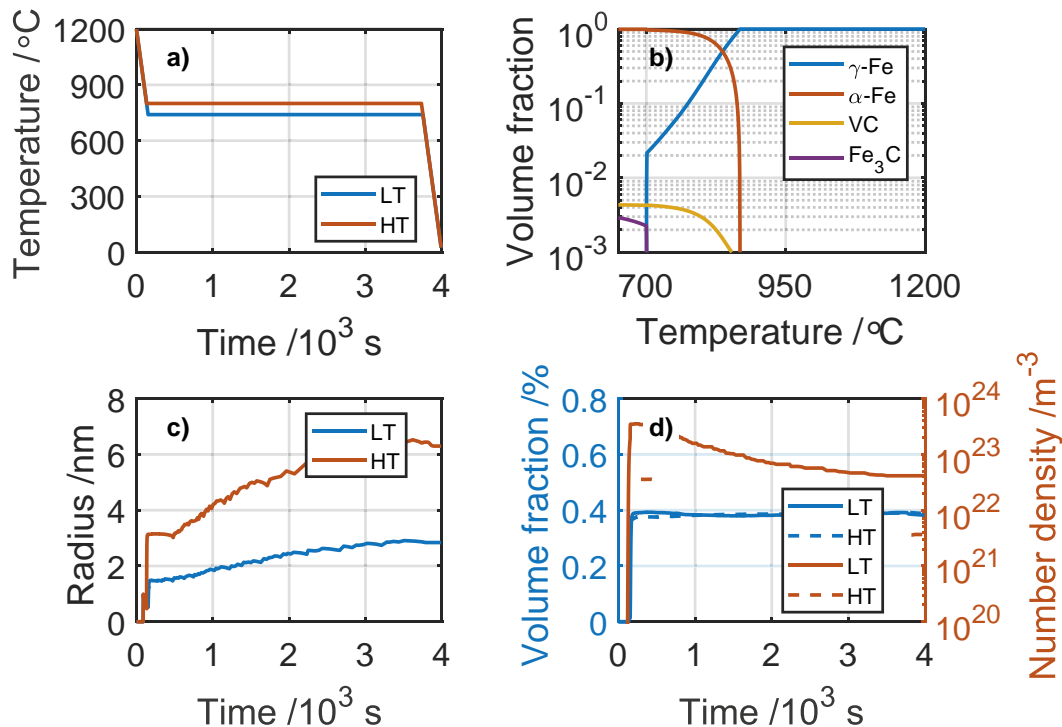


Fig. 1. Simulation results – a) heat treatments, b) phase stability diagram, c) radii and d) number density/volume fractions.

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